

Moisture induced Ageing in Granular Media

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We present experiments showing that a granular system of small beads does exhibit ageing properties : its maximum stability angle is measured to increase logarithmically with resting time, *i.e.*, the time elapsed before performing the measure. We show that humidity is the crucial ingredient responsible for this behaviour : while ageing effects are important at intermediate humidity, they disappear at vanishing humidity. On the basis of these experimental results, we propose a model based on the activated condensation of liquid bridges between the beads. Within this picture, we are able to reproduce both the waiting-time and humidity dependence of the ageing properties.

In his pioneering treatise published in 1773 [1], Charles de Coulomb pointed out the peculiar properties of granular systems. His decisive remark was to recognize the links existing between the statics of granular systems and the friction properties of two solids at contact : the equilibrium and stability of granular edifices could be discussed in terms of the friction between the different part or layers of the system [2]. In particular, he deduced a relationship between the rest angle of the pile, θ_0 , and the static friction coefficient μ_s of the medium, in the form $\tan \theta_0 = \mu_s$. One knows by now that this relation is only a good first approximation and that a wide variety of behaviours can be observed in granular systems [2]. The same is true for dry friction problems : while the subject remained poorly understood during more than 150 years, a lot of new results emerged in the last four decades.

In particular, one of the intriguing behaviour of friction is the existence of ageing properties of the static friction coefficient, μ_s : the latter is found to increase logarithmically with resting time, *i.e.*, with the time during which the system was left at rest before pulling it (in order *e.g.* to probe μ_s). Now, if Coulomb’s analogy between solid friction and the statics of granular systems is further pursued, a question arises : can ageing be observed in granular systems too ?

In order to verify this assertion, we have studied the effect of waiting time on the angle of first avalanche θ_w of a granular system of small (typically $200\mu m$) spherical glass beads contained in a rotating drum, following a protocole described in fig. 1.a. Astonishingly, and in close analogy with dry friction, a logarithmic ageing of the maximum static angle θ_w is observed, as shown in fig. 2.a. In other words, granular media exhibit ageing. The dependence on bead size has been studied and ageing was not observed for beads with a diameter larger than 0.5 mm , except for very large humidities. On the other hand it is known that humidity is an important parameter in the description of granular media [2]. Addition of small quantities of wetting liquid has been shown to change enormously the repose angle of a pile [3] ; a brief discussion of moisture effects can even be found in Coulomb’s treatise [1]. We thus repeated the experiments for various humidities P_v/P_{sat} . As shown on figure 2.b, humidity appears to be the **crucial parameter** which controls the ageing of θ_w : no ageing is observed for small humidity, while the “strength” α of the ageing effect increases in an enormous way with humidity.

This humidity dependence leads to the intuitive idea that the ageing effects originate from the condensation of small liquid bridges between the beads. Indeed, liquid bridges induce a significant cohesion force between the beads, which can increase the friction between different layers of the granular system and result in a higher value of θ_w . However, the physical justification of this intuitive behaviour is not obvious at all. Let us first consider the idealized situation of two smooth beads in contact : the capillary adhesion force exerted

by a small liquid bridge connecting the beads is given by the product of the liquid surface tension times the radius of the beads ¹ : $F_{adh} \sim 2\pi\gamma R$, whatever the size of the (small) bridge [5]. Therefore, the adhesion force has no humidity dependence, and would be moreover able to stick all beads together [2]. This apparent difficulty disappears if one takes into account the roughness of the beads. At the liquid-vapour equilibrium, the radius of curvature r_{eq} of the liquid meniscus is fixed by the so-called Kelvin relation [6]

$$\frac{\gamma}{r_{eq}} = \rho_l k_B T \log \frac{P_{sat}}{P_v} \equiv \rho_l \Delta\mu \quad (1)$$

where ρ_l is the density of the liquid and the ratio $\frac{P_v}{P_{sat}}$ defines humidity. Under ambient conditions, this yields a nanometric order of magnitude for r_{eq} ! A crucial consequence is that liquid bridges are able to form only in **nanometric interstices**. Because the beads are not smooth at the nanometer scale, the wetted region does not spread over the whole possible area it would occupy if the beads were smooth, and the cohesive force is reduced in proportion. Another counter-intuitive behaviour is the slow evolution in time of the cohesive properties, measured through the time dependency of θ_w . This indicates that condensation of liquid bridges takes place over very long time scales. This feature is in agreement with experiments using Surface Force Apparatus (SFA) and AFM techniques [7], which show that an interstice between two solid surfaces can remain for a very long time in a **metastable** dry state while the equilibrium state would be a condensed liquid bridge.

On the basis of all these considerations, we propose a model based on the condensation of interstitial liquid bridges via an **activated process**. In this letter, we shall only outline the main features of the physical mechanism and a more detailed presentation will be published elsewhere by the authors. Let us consider two “rough” beads at contact. Under the assumption of an activated process, the time needed in order to condense a liquid bridge in

¹The following expression assumes that solids do not deform because of the capillary force. If solid deformation occurs, the numerical prefactor changes slightly [4].

an interstitial volume is $\tau \simeq \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right)$, with τ_0 a microscopic time and ΔE an activation energy barrier. Nucleation occurs preferentially at the level of a nano-asperity, and the activation energy is accordingly $\Delta E \sim \Delta\mu \rho_l a_0^2 e$, where $\Delta\mu = \mu_{sat} - \mu_g \simeq k_B T \log(P_{sat}/P_v)$, ρ_l is the density of the liquid, e the gap between the surfaces at the level of the nucleating site and a_0^2 a typical nucleation area (see fig. 1.b). Now, since both beads are rough, one expects the nucleating sites to exhibit a broad statistics of gaps e between solid surfaces and the activation times are accordingly widely distributed. After a given time t_w , only the bridges with an activation time τ_{act} smaller than t_w have condensed. These were therefore formed at the nucleating sites with a gap e verifying $e < e_{max}(t_w) = \frac{k_B T}{\Delta\mu} \frac{1}{\rho_l a_0^2} \log\left(\frac{t_w}{\tau_0}\right)$. Once a liquid bridge has condensed, it fills locally the volume surrounding the nucleating site, until the Kelvin equilibrium condition for the radius of curvature, eq. (1), is met. Thus, because of roughness, only a part of the total wettable area is indeed wetted at a given time t_w . The corresponding fraction $f(t_w)$, is proportionnal to the number of activated bridges, yielding in first approximation $f(t_w) \sim e_{max}(t_w)/\lambda$, with λ the typical width of the distribution of distances between the surfaces. The capillary adhesion force is thus reduced by the same factor as compared to the perfectly smooth case, leading to

$$F_{adh}(t_w) \simeq \gamma d \frac{1}{\log \frac{P_{sat}}{P_v}} \log\left(\frac{t_w}{\tau_0}\right) \quad (2)$$

where $d = 2\pi R/(\lambda \rho_l a_0^2)$ is a distance taking into account the geometrical characteristics of the contact. Now, by reproducing Coulomb's argument for the stability of the surface layer in the presence of this additional adhesive force, one obtains the following implicit equation for $\theta_w(t_w)$:

$$\tan \theta_w(t_w) \simeq \tan \theta_0 + \frac{\alpha(P_v)}{\cos \theta_w(t_w)} \log\left(\frac{t_w}{t_0}\right) \quad (3)$$

with $\alpha(P_v) = \alpha_0 / \log \frac{P_{sat}}{P_v}$ and α_0 is a numerical constant depending on the characteristics of the beads. Thus, by plotting $\tan \theta_w(t_w)$ as a function of $\log(t_w) / \cos \theta_w(t_w)$, one should obtain a straight line : as shown on fig. 2.a, this expectation is indeed in very good agreement

with experimental results. Moreover, as exhibited on fig. 2.b., the increase of the slope, $\alpha(P_v)$, of this line with humidity is in good agreement with the theoretical prediction eq. (3). Our model is thus able to reproduce both the waiting-time and humidity dependence of the measured ageing properties of a granular system.

Our results highlight the crucial role of humidity in the statics of granular systems. We have shown that the latter do exhibit ageing properties in an analogous way to those encountered in dry friction for the static friction coefficient μ_s . The analogy is in fact even more striking, since a similar effect of humidity has been reported in friction between rocks [8], though not extensively studied : in ref. [8], the “standard” ageing properties of μ_s were found to disappear at vanishing humidity, just like in the case of a granular system ! Similar behavior were even observed in indentation experiments too [9]. It would be thus interesting to check to which extent the analogy between dry friction and granular media is indeed pertinent. The hope is to propose an alternative understanding for the ageing properties observed in solid friction.

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REFERENCES

- [1] Coulomb, Sur une application des règles de Maximis et Minimis à quelques Problèmes de Statique, relatifs à l'Architecture, in *Mémoires de Mathématiques et de Physique, Académie Royale des Sciences, Paris*, 343-382 (1773).
- [2] J. Duran, *Sables, Poudres et Grains* (Eyrolles Sciences, Paris, 1997).
- [3] D.J. Hornabaker, R. Albert, I. Albert, A.-L. Barabasi, P. Schiffer, What keeps sandcastles standing ?, *Nature*, **387**, 765 (1997).
- [4] D. Maugis, Adhesion of Spheres : The JKR-DMT Transition using a Dugdale Model, *J. Colloid and Interface Sci.*, **150**, 243-269 (1992).
- [5] J.N. Israelachvili, *Intermolecular and Surfaces Forces* (Academic Press, London, 1985).
- [6] R. Evans, Microscopic Theories of simple fluids and their interfaces, in *Liquids at Interfaces*, J. Charvolin, F.F. Joanny and J. Zinn-Justin, eds. (Elsevier Science Publishers B.V., 1989).
- [7] Crassous J., Charlaix E. and Loubet J.-L., Capillary Condensation between High-Energy Surfaces. An experimental study with a Surface Force Apparatus, *Europhys. Lett.* **28**, 37-42 (1994).
- [8] J. Dieterich and G. Conrad, Effect of Humidity on Time- and Velocity-Dependent Friction in Rocks, *J. Geophys. Res.* **89**, 4196-4202 (1984).
- [9] J.H. Westbrook and P.J. Jorgensen, Effect of Water Desorption on Indentation Micro-hardness Anisotropy in Minerals, *The American Mineralogist* **53**, 1899-1914 (1968).

Figure 1.a : Description of the experimental setup. The glass beads fill 25 % of the volume of a cylinder (diameter 100 mm, thickness 13 mm) which can rotate around its axes. Two different systems have been extensively studied, a “polydisperse” one, $140\mu m < d < 260\mu m$ and a “monodisperse” one $200\mu m < d < 250\mu m$, d being the diameter of the beads. The walls of the cylinder are made of glass, and the shape of the bead’s pile is recorded with a video camera. Experiments are performed at room temperature, under controlled humidity (defined as the ratio between the vapour and saturated pressure of water, P_v/P_{sat}). Before starting experiments, the system is prepared by rotating the drum during approximatively 12 hours. Then the ageing properties are investigated for various values of P_v/P_{sat} using the following protocol : (i) first, the system is put in motion for a few turns (typically three); (ii) the end of this “motion period” defines the origin of waiting time $t_w = 0$, after which the system is left at rest; (iii) after a given time (ranging from 10 to 10^4 seconds), a slow rotational motion (with velocity less than one turn per minute) is transmitted to the cylindrical drum. The angle θ_w at which the first avalanche takes place is measured from the slope of the beads just before the avalanche. The same procedure is repeated for different waiting times t_w and a whole curve θ_w *vs.* waiting time t_w can be constructed.

Figure 1.b : Schematic drawing of the contact at the nanometer scale between two micrometric asperities on the beads. Inside most of the contact region, the solid surfaces do not really touch eachother at the molecular scale, and capillary condensation occurs in the interstice left between the surfaces.

Figure 2.a : Logarithmic ageing of the angle of first avalanche. As explained in the text after eq. (3), the ageing property is best analysed by plotting $\tan\theta_w(t_w)$ as a function of $\log_{10}(t_w)/\cos\theta_w(t_w)$, for different values of the water vapor pressure P_v . From bottom to top, humidity is : 15% (triangles), 27% (pentagons), 36.1% (squares) and 45.5% (circles). In these measurements, times runs typically over the range $t = 5$ s up to $t = 5000$ s. The dotted lines are least-square fits of the experimental data, whose slope is identified with

$\alpha(P_v)$.

Figure 2.b : Variation of the slope $\alpha(P_v)$ characterizing the ageing behavior of the first avalanche angle (see text eq. (3)) with humidity P_v/P_{sat} . Open dots correspond to the polydisperse system, and filled dots to the monodisperse one. The dashed line is the theoretical prediction $\alpha = \alpha_0 / \log(P_{sat}^*/P_v)$, where $\alpha_0 = 0.079$ and $P_{sat}^* = 0.68 P_{sat}$. The validity of the previous theoretical prediction is best confirmed by the measured linear dependence of $1/\alpha$ as a function of $\log(P_{sat}/P_v)$ (see inset) : in this plot, a linear least-square fit thus provides unambiguously both values of α_0 and P_{sat}^* . The lowering observed in the saturating pressure P_{sat}^* might be an effect of the long-ranged attraction forces exerted by the walls, and/or of dissolved species in condensed water.

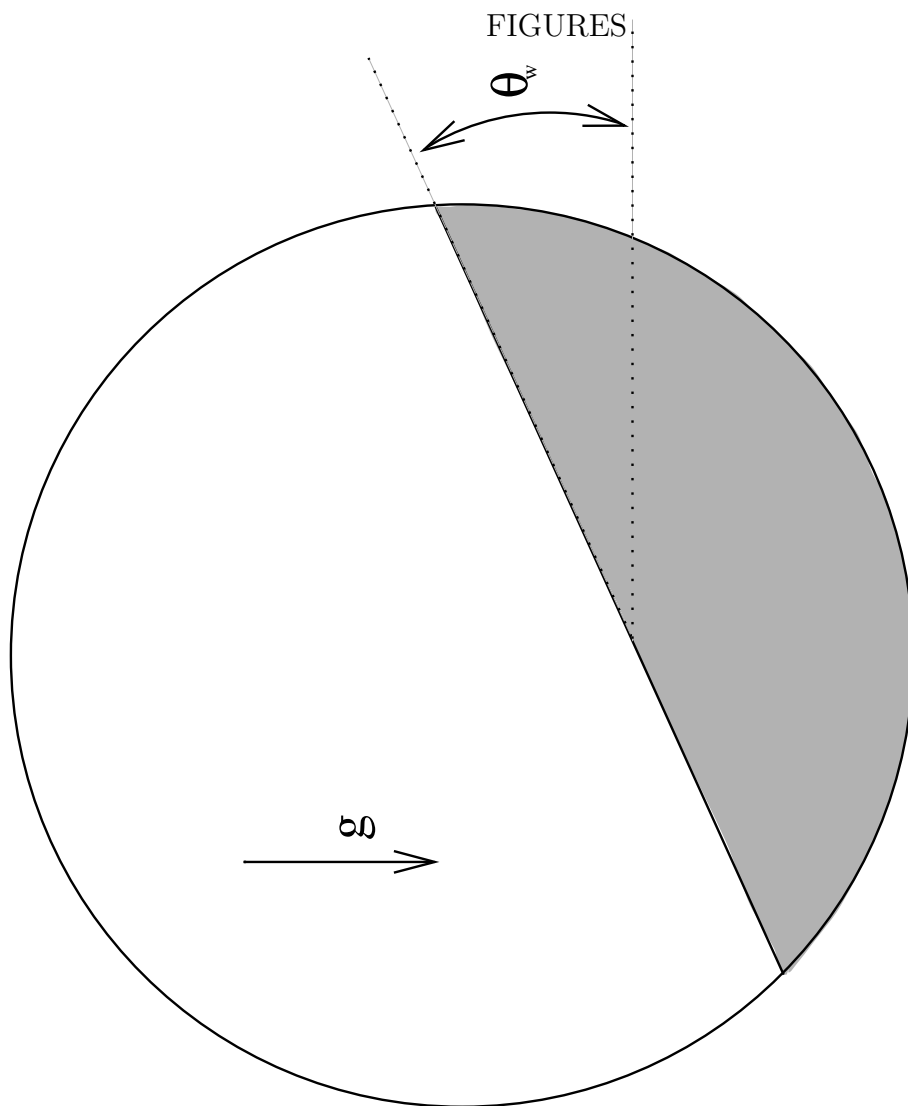


Figure 1a. Moisture induced Ageing in Granular Media

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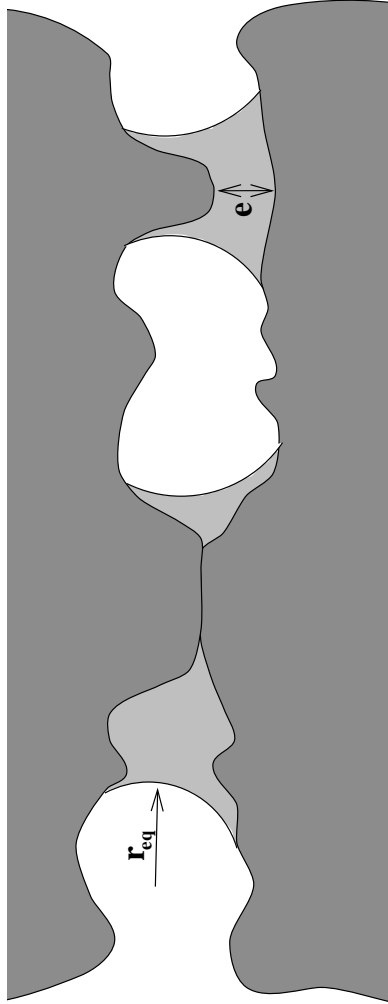


Figure 1b. Moisture induced Ageing in Granular Media

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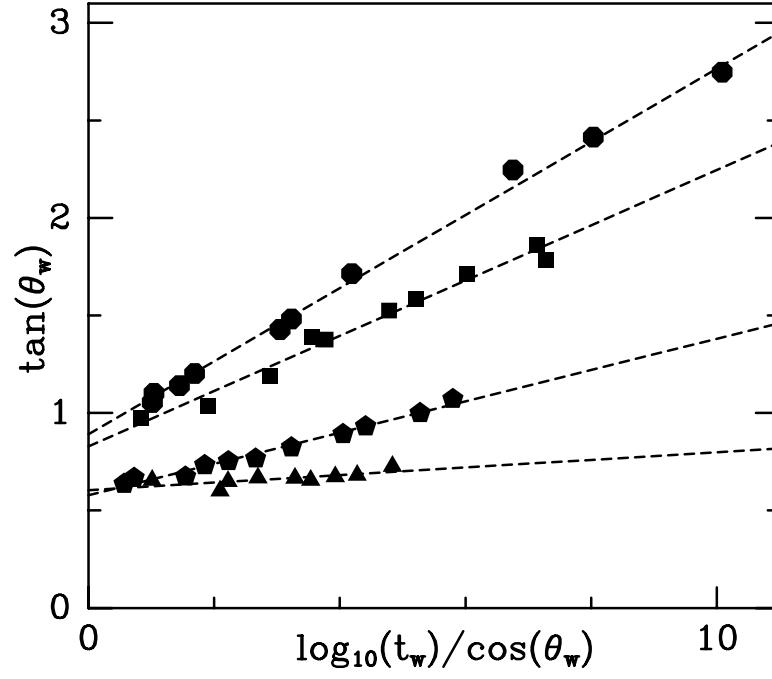


Figure 2a. Moisture induced Ageing in Granular Media

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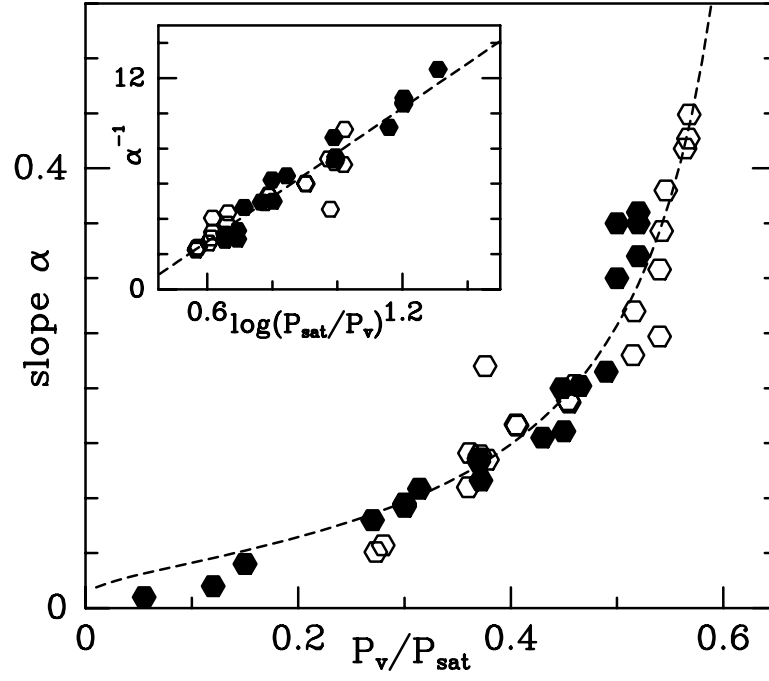


Figure 2b. Moisture induced Ageing in Granular Media

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